CATALYTIC COMBUSTION OF VOC IN AIR STREAM OVER BIMETALLIC CHROMIUM-COPPER SUPPORTED ON $SICL_4$-MODIFIED H-ZSM-5 CATALYST

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Abstract : The performance of chromium (Cr) and copper (Cu) on silicon tetrachloride modified H-ZSM-5 (SiCl4-Z) catalyst in VOC combustion is reported. H-ZSM-5, modified with SiCl4 at 500°C for 3 h was impregnated with 1.0 wt. % of Cr and 0.5 wt. % of Cu. Performance studies were carried out at GHSV of 3,800 to 32,000 h-1 with 2,000 to 35,000 ppm of VOC. Changes in the activity of Cr-Cu/SiCl4-Z were ascribed to extra framework deposits, surface acidity and pore characteristics. Cr-Cu/SiCl4-Z catalyst was more stable to coking, humidity and HCl than Cr-Cu/Z. In the combustion of chlorinated VOC, the chlorination of metal species deactivated the catalyst by rendering lower redox ability.

Keywords: H-ZSM-5 ; $SiCl_4$; VOC ; activity ; deactivation ; stability.

1. INTRODUCTION

Volatile organic compounds (VOCs) are important environmental pollutants and catalytic combustion is a viable technology for the removal of these compounds in air [1]. An ideal catalyst for VOC combustion should have high activity, high carbon dioxide yield, high hydrothermal stability, low coking activity and most importantly, produced at low cost [2]. In the combustion of chlorinated VOC (Cl-VOC), hydrogen chloride, and sometimes, molecular chlorine (Cl_2) that are produced can cause rapid deactivation of the catalyst [3]. A combination of chromium and copper was found to produce a catalyst with high activity and high carbon dioxide yield while, showing lower coking tendency [4]. $SiCl_4$ treatment was found to increase the hydrophobicity of H-ZSM-5 while suppressing coking activity [5]. Therefore, it is of interest to study the activity of Cr-Cu/$SiCl_4$-Z catalyst in the combustion of VOC. Ethyl acetate (EAc), benzene (Bz), trichloromethane (TCM) and trichloroethylene (TCE) were used due to the differences in their chemical nature, reactivity, molecular weight and chlorine content. The deactivation of the catalyst was scrutinized on the basis of the physicochemical changes occurred on the active metal species and the catalyst support to identify the more dominant deactivation mechanism.

2. EXPERIMENTATION

2.1. Preparation of the Catalyst

The ZSM-5 (Si/Al=240) zeolite sample was supplied by Süd-Chemie AG in its sodium form. H-ZSM-5 (coded H-Z) was prepared through exchanging the Na^+ cation by NH_4^+ followed by calcination. The chemical modification of H-ZSM-5 was performed by reacting the H-ZSM-5 sample with silicon tetrachloride vapor, followed by acid leaching, filtration, washing and drying. The detail procedures for the preparation of H-Z and $SiCl_4$-Z are available in literature [4,6]. The unmodified and modified H-ZSM-5 supported bimetallic chromium-copper catalysts were prepared via the impregnation method by the procedure described by Zuhairi et al. [5]. These catalysts were coded as Cr-Cu/Z and Cr-Cu/$SiCl_4$-Z, respectively.

2.2. Catalyst Characterization

The catalyst samples were analyzed for surface characteristics using the Quantachrome Autosorb-1, crystallinity using a Siemens D2000 X-ray diffractometer, acidity and temperature programmed reduction profile using the Chembet 3000 system, coke content using a Perkin Elmer TGA7 and infrared absorbance using a Perkin Elmer 2000 FT-IR system. Details on the experimental conditions are available in our previous reports [4,5].

2.3. Catalyst Performance Studies

The performance studies of the catalyst were carried out using catalytic reactor as described in our previous report [7]. The performance of the catalyst was assessed on the basis of the conversion determined at a gas hourly space velocity (GHSV) of 32,000 h^{-1}. The feed VOC concentration used was 2,000 ppm for ethyl acetate and benzene and, 2,500 ppm of TCM and TCE.In order to prepare aged catalyst samples, feeds containing 32,000 ppm of ethyl acetate and benzene or, 35,000 ppm of TCM and TCE were passed through the reactor at a reaction temperature of 400°C and a GHSV of 3,800 h^{-1}. The reaction rate over the catalyst was determined by operating the reactor in a differential mode at a GHSV of 78,900 h^{-1} at 400°C. The activity (a) of the catalyst was taken as the ratio between reaction rates at time t to that of fresh catalyst.

2.4. Resistance of H-ZSM-5 Support Against Gaseous HCl

The resistance of the modified and unmodified H-ZSM-5 support against hydrogen chloride was demonstrated using the method proposed by Kulażyński *et al.* [6]. First, the support material was heated in the reactor at 400°C while an air flow at 50 ml/min was passed through the reactor for 4 h. This air stream was previously passed through a saturator containing concentrated HCl.

3. RESULTS AND DISCUSSION

3.1. Characteristics of the Catalysts

Table 1 summarizes important characteristics of the catalysts used in this study. Changes in micropore area can qualitatively indicate the degree of modification of the zeolite framework as it constituted about 80 % of total surface area of the unmodified H-ZSM-5

support. Cr-Cu/$SiCl_4$-Z showed higher drop in the surface area. The mesopore area of this catalyst constituted about 39 % of the total surface area compared to that of Cr-Cu/Z which was about 23 %. Cr-Cu/$SiCl_4$-Z also experienced more drop in crystalinity, indicating that significant defects had occurred in the H-ZSM-5 framework and the presence of non-framework silicon deposits [5].

Table 1 Characteristics of the catalysts used.

Properties	[a]Material		
	H-Z	Cr-Cu/Z	Cr-Cu/$SiCl_4$-Z
BET Surface area (m^2/g)	386	360	324
Micropore area (m^2/g)	315	278	198
Mesopore area (m^2/g)	71	82	126
Metal loading (wt.%)	-	1 % Cr and 0.5 % Cu	
[b]Crystallinity (%)	100	95	66
Acidity (mmol NH_3/g)	0.22	0.17	0.09

[a]Z=H-ZSM-5(Si/Al=240)
[b]Relative to H-ZSM-5

Impregnation of chromium and copper on H-ZSM-5 appeared to weaken the overall acidity from 0.22 mmol NH_3/g to 0.17 mmol NH_3/g, attributed mainly to the masking of acid sites by metal deposits. Cr-Cu/$SiCl_4$/Z experienced more reduction in the acidity, i.e. by 0.13 mmol NH_3/g as the extraction of aluminum atoms from the framework eliminated some of the acid sites while silicon deposition could mask some of the remaining acid sites [8]. The presence of silicon deposits in this catalyst caused significant reductions in BET surface area, and an increment in micropore area and mesopore area, respectively compared with those of the Cr-Cu/Z.

3.2. Activity Study

Fig. 1 depicts the profiles of conversion with temperature for ethyl acetate and benzene as non-chlorinated VOC model compounds. At low temperatures (below 250°C), Cr-Cu/Z was the more active catalyst for both organics. However, at higher temperatures, both catalysts produced almost similar activity where complete combustion of ethyl acetate was achieved above 350°C. Benzene was clearly a relatively more stable organic and could not be totally converted below 500°C.

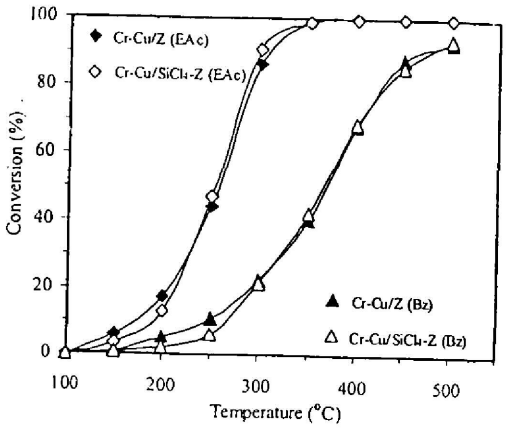

Fig. 1: Combustion of ethyl acetate (EAc) and benzene (Bz) over Cr-Cu/Z and Cr-Cu/$SiCl_4$-Z. (C_{voc}=2,000 ppm, GHSV=32,000 h^{-1}).

At low reaction temperatures, the activity of the two catalysts was mainly governed by their pore characteristics and the length of diffusion pathways. Due to less geometric constraint in mesopores [9], chromium and copper could grow to bigger crystallites, resulting in lower metal dispersion. Pore narrowing by extra framework species also caused some diffusion limitation [10] in Cr-Cu/$SiCl_4$-Z, resulting in lower conversion. However, at high temperatures (above 250°C), there was no clear difference between the activity of Cr-Cu/Z and Cr-Cu/$SiCl_4$-Z as the rate of the oxidative reaction was sufficiently fast to offset negative effects correlated with the surface characteristics of Cr-Cu/$SiCl_4$-Z catalyst.

Similar explanation applies for the slightly lower activity observed at low reaction temperatures with Cr-Cu/$SiCl_4$-Z as compared to Cr-Cu/Z in the combustion of chlorinated VOCs (Fig. 2). In general, TCM and TCE were more reactive compared to benzene with conversions exceeding 90 % above 400°C. Regardless of catalyst used, TCE was found to be more stable than TCM, attributed to the occurrence of a resonance effects in the molecule from interactions between lone pair electron in chlorine atoms and the π electron in the C=C double bond. First, the more electronegative chlorine atoms pulled electrons from the π system of the C=C double bond. Conversely, lone pairs of electrons from the chlorine were extended to the new π-bonding in the C=Cl bond by donating some electrons back to the π system [11]. This interaction was possible as the electronic configuration of an atom of chlorine is $1s^2 2s^2 2p^6 3s^2 3p^5$ and the σ-bond formation with the carbon atom left one diagonal lone pair ($3s^2$) and two p-orbital lone pairs ($3p_{xy}^2$ and $3p_{yz}^2$) in the valence shell. One of these lone pairs was free to overlap with the π-bond (of the C=C entity) to give an extended π-electron system [12].

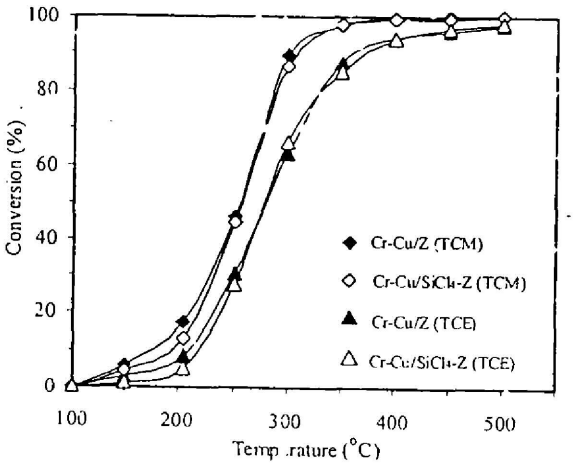

Fig. 2: Combustion of trichloromethane (TCM) and trichloroethylene (TCE) over Cr-Cu/Z and Cr-Cu/$SiCl_4$-Z (C_{voc}=2,500 ppm, GHSV=32,000 h^{-1}).

3.3. Resistance Against Gaseous HCl

As hydrogen chloride (the desired chlorinated product in the combustion of Cl-VOC) can pose significant problems to the catalyst, chemical resistance of the SiCl4-Z support and H-Z (control) to hydrogen chloride was also tested. As shown in Table 2, the treatment with hydrogen chloride had a minimal effect on BET surface area and micropore surface areas of SiCl4-Z with a high crystallinity retention of over 90 % by both materials. SiCl4-Z had an improved stability against hydrogen chloride as indicated by a higher

crystallinity retention. Table 2 also evidences that hydrogen chloride mainly affected weak acid sites with reductions of between 52 and 58 % while the effect on strong acid sites were limited to below 8 %.

Table 2: Changes in characteristics of Z and $SiCl_4$-Z after treatment with gaseous hydrogen chloride at 400°C for 4 h.

Characteristics	[a]Support			
	Fresh Z	[d]Treated Z	Fresh $SiCl_4$-Z	[d]Treated $SiCl_4$-Z
BET surface area (m^2/g)	386	368	346	340
Micropore area (m^2/g)	315	290	211	204
Mesopore area (m^2/g)	71	78	134	136
[b]Strong acidity (mmol NH_3 /g)	0.121	0.112	0.045	0.042
Weak acidity (mmol NH_3 /g)	0.099	0.042	0.063	0.030
[c]Crystallinity (%)	100	91	100	96

[a] Z=H-ZSM-5(Si/Al=240)
[b] Sites retaining ammonia at temperatures higher than 250°C
[c] Relative to respective fresh support
[d] After reaction with gaseous HCl at 400°C for 4 h

The high resistance of H-Z against hydrogen chloride was mainly ascribed to its high Si/Al ratio since Si-O bonds were stronger and more resistant to hydrolytic and acid attacks than the Al-O bonds [13]. The higher bond strength was attributed to the smaller atomic size and higher electronegativity of Si atoms compared to Al, thus resisting electron polarity in its chemical bond [12]. The introduction of more silicon atoms into the framework after the silicon tetrachloride treatment also caused partial replacement of framework aluminum atoms [4]. The effect manifests itself in a further improvement of the resistance against hydrogen chloride as showed by SiCl4-Z.

3.4. Deactivation Study

In the present study, the combustion of ethyl acetate was generally found to cause more coking and subsequently, more catalyst deactivation compared to that of benzene. Thus, the stability of the catalysts was demonstrated by ageing them with 32,000 ppm of ethyl acetate at 400°C for 12 h. As shown in Table 3, Cr-Cu/$SiCl_4$-Z showed higher stability in terms of conversion retention than Cr-Cu/Z in both dry and humid conditions. The lower tendency to coking in humid conditions was due to lower catalytic activity resulting from competitive adsorption between organic and water molecules on active sites. Consequently, fewer precursors were produced to participate in the coke formation process [4]. The humid ageing test affected the H-ZSM-5 framework as all of the catalyst studied experienced reduction in crystallinity after the treatment. The effect was attributed to the hydrolysis of Si-O-Si and Si-O-Al bonds in the H-ZSM-5 framework. Owing to higher affinity of Si atoms towards electrons, O-Si bonds were relatively more resistant to hydrolytic cleavage than O-Al bonds [1]. Therefore, Cr-Cu/$SiCl_4$-Z demonstrated higher hydrothermal stability due to a lower aluminum content in their framework and higher hydrophobicity to resist the effects of water. Since the effect of treatment of H-ZSM-5 with silicon tetrachloride was more favored on the external surface [4], partial elimination of external Brønsted acid sites resulted. External coke was known to be more toxic to the catalytic activity [1]. Thus, a decrease in the number of external Brønsted acid sites resulted in a more stable catalyst especially under dry conditions where coking was the main cause

of deactivation. This was not observed under humid conditions where other mechanisms made a significant contribution to deactivation.

Table 3: Summary of changes occurred after exposure to 32,000 ppm of ethyl acetate at 400°C for 12 h.

Properties	[a]Condition	Catalyst	
		Cr-Cu/Z	Cr-Cu/$SiCl_4$ Z
[b]Activity, *a*	Dry	0.91	0.95
	Humid	0.85	0.89
Coke content (wt.%)	Dry	8.8	7.2
	Humid	6.4	5.2
[c]Crystallinity (%)	Dry	80.8	93.6
	Humid	71.2	88.6

[a] Humid condition contains 9,000 ppm H_2O.
[b] $a = -r'_i/-r'_o$ (measured with 2,000 ppm ethyl acetate at 400°C).
[c] Relative to respective fresh catalysts.

Profiles of catalysts deactivation with time after ageing with different feed of Cl-VOCs are shown in Fig. 3. The profiles were characterized by an initial sharp drop followed by a gradual decrease in the activity until a relatively stable activity was reached at a longer operation time. The Cr-Cu/$SiCl_4$-Z catalyst appeared to be more resistant to deactivation with less than 15 % activity drop detected for both types of chlorinated organics. Compared to TCM, TCE showed an initially slower deactivation, but as the time progresses, a larger activity drop was experienced by the catalyst

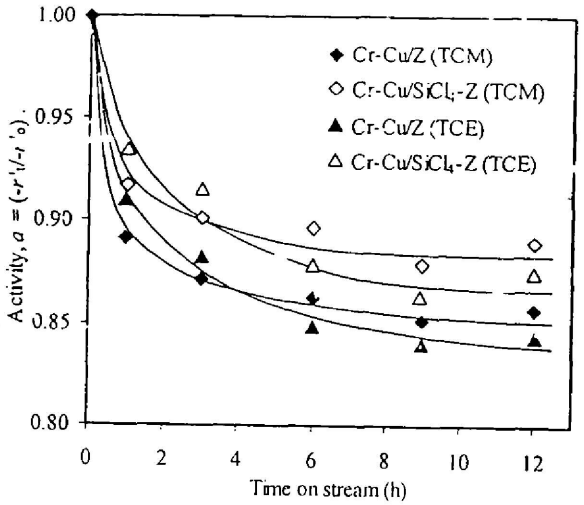

Fig. 3: Deactivation of Cr-Cu/Z and Cr-Cu/$SiCl_4$-Z catalysts in the combustion of trichloromethane (TCM) and trichloroethylene (TCE). (C_{voc}=35,000 ppm, GHSV=3,800 h^{-1}, T=400°C).

Upon completion of the ageing test, the coke deposition on the catalyst was found to be very minimal with less than 1 wt. % TCM, and 1.8 wt. % for TCE. Thus, it could be concluded that the catalyst deactivation was mainly attributed to the interactions between the catalyst and chlorine, bearing in mind that the SiCl4-Z support was highly resistant to hydrogen chloride. Low coking activity with TCM was ascribed to their small molecules and highly reactive intermediates to give high selectivity to gaseous products [3]. With

increasing molecular size in TCE, the coking activity increases but is still low compared to that of ethyl acetate (Table 2). Initial interactions between metallic species and chlorine atoms to form metal chloride caused rapid deactivation of the catalyst as indicated by a steeper drop in the activity. Then, a more stable activity was obtained suggesting a limited capacity of the metallic species to receive chlorine. By theory, highly stable Cr^{3+} can only receive three chlorine atoms to form chloride while it is two atoms with Cu^{2+}. However, with the ability of chromium and copper to present at multiple oxidation states, coupled with the ability of molecular chlorine to act as strong oxidizing agentthese interactions became more complicated. This was probably the governing factor characterizing the deactivation profile of the catalyst with time.

TCM, with higher chlorine content in its molecule caused more deactivation compared to dichloromethane (DCM). This was due to the higher reactivity of TCM to consequently cause more chlorination of the active metal species. In fact, the H/C ratio of the Cl-VOC was the key factor that determined the life of a combustion catalyst [6]. In a similar way, the initial slower activity decay with TCE compared to that caused by TCM could be attributed to the lower reactivity of the former substance. However, at longer operating times, TCE caused more deactivation as the coke significantly affected the process.

3.5. Effects of Ageing on Surface Hydroxyl Groups

In zeolites, surface hydroxyl groups fall under two major groups viz. bridging hydroxyl belonging to Brønsted acid sites and silanols associated with a wide infrared absorption band centered at 3,595 cm^{-1} and 3,735 cm^{-1}, respectively [14]. Since the infrared absorption spectra for these two types of hydroxyl groups did not show well-separated peaks (Fig. 4), qualitative comparison between the samples was based on the shape of the peaks between 3,300 cm^{-1} and 3,800 cm^{-1}.

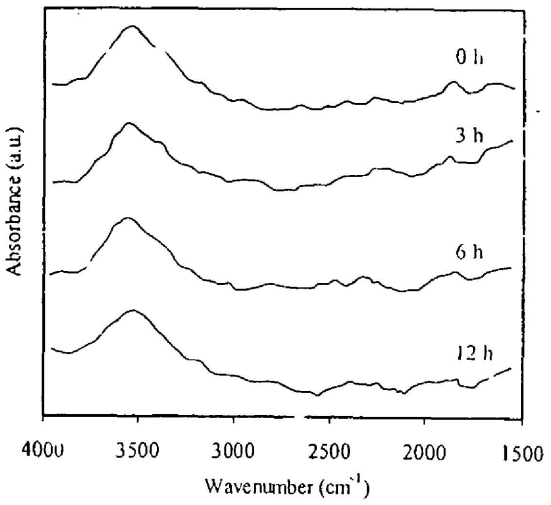

Fig. 4: Infrared absorbance of Cr-Cu/$SiCl_4$-Z after ageing with 35,000 ppm of TCE at 400°C for four different times on stream.

Figure4 shows that the hydroxyls absorption region was characterized by almost symmetrical peaks between 3,300 cm^{-1} and 3,800 cm^{-1}. When the Cr-Cu/$SiCl_4$–Z catalyst was deactivated with time, a minimum reduction in the intensity of the peak was detected but the basic shape of the peak remained unchanged. Changes in the shape of the

absorption profile upon ageing with TCE suggested a non-selective elimination of both bridging hydroxyl and silanol with time.

If there were chemical interactions between Si or Al atom with chlorine, it should be in favor of Al and lead to the disappearance of bridging hydroxyl groups. This is based on the fact that the Al atom with an outer electron configuration of $3s^2\ 3p^1$ can more readily donate its electron to form aluminum chloride. The corresponding loss of strong acid sites should be the other consequence. However this loss was not observed through the acidity study on $SiCl_4$-Z upon ageing with hydrogen chloride. This result thus led to the general conclusion that hydroxyl groups on the surface of Cr-Cu/$SiCl_4$–Z were not chemically altered during the combustion of Cl-VOCs. The disappearance of hydroxyls upon ageing with TCE might be due to physical means such as coking rather than chemical interactions. All these findings led to the conclusion that the $SiCl_4$-Z was sufficiently stable to resist deactivating effects during the combustion of chlorinated VOC.

3.6. Temperature programmed Reduction (TPR) Profiles of Aged Cr-Cu/$SiCl_4$-Z

As the $SICl_4$-Z support was found to be virtually unaltered chemically upon ageing with TCE, effort was made to characterize the deactivation of Cr-Cu/$SiCl_4$-Z catalyst on the basis of changes occurred on its active metal species. For this purpose, a TPR analysis was performed on the catalyst. The TPR profile of fresh Cr-Cu/$SiCl_4$-Z was characterized by two major peaks occurring at different temperature regions (Fig. 5). The peak at around 380°C was assigned to the combined reduction of Cr^{6+} and Cu^{2+} while the second peak occurring at about 480°C was attributed to the reduction of Cr^{3+} and Cu^{+} [4]. Upon ageing with TCE, the first peak appeared to be eliminated with time while the overall reducibility of the metal species on the catalyst decreased. The TPR result suggested that chlorination weakened the overall reducibility of the active metals. This could be due to high electronegativity of chlorine atom that formed stronger ionic bond in metal chloride to pose more resistance to reduction during the TPR analysis. The shape of the peak in the TPR profile upon ageing with TCE suggested that the first peak was more selectively eliminated. More favorable redox reactions between Cr^{6+} and Cu^{2+} with chlorine producing oxychlorides or molecular chlorine (Cl_2) leading to the reduction of these metal species was deemed as the main factor behind this result. The main peak in the TPR profile of aged catalyst must be mainly attributed to the combined reduction of Cr^{3+} and Cu^{+} Changes in the activity due to changes in the reducibility of the metal species in the catalyst could be explained by the Mars-van Krevelen model. With the chlorination of metal species in Cr-Cu/$SiCl_4$-Z, metal chlorides were formed. These chlorides were more resistance to reduction and an overall reduction in redox activity of the catalyst resulted. According to the Mars-van Krevelen model, a decrease in the overall activity of the catalyst was the likely consequence.

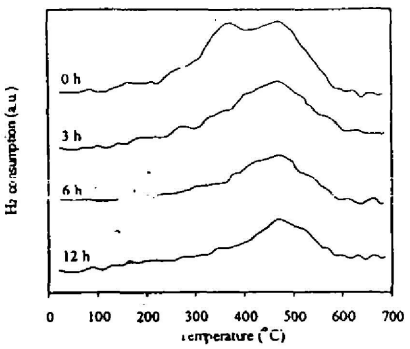

Fig. 5 TPR profiles of Cr-Cu/$SiCl_4$-Z catalyst after ageing with 35,000 ppm of TCE at 400°C for four different times on stream.

4. CONCLUSIONS

The presence of catalyst was found to significantly improve the rate of VOC combustion, causing reduced operating temperature requirement to achieve high conversion. Changes in the activity of Cr-Cu/$SiCl_4$-Z as compared to that of Cr-Cu/Z, occurred especially at low temperatures and were ascribed to extra framework deposits, surface acidity and pore characteristics. At high temperatures (above 250°C), there was no clear difference between the activity of Cr-Cu/Z and Cr-Cu/$SiCl_4$-Z as the rate of the oxidative reaction was sufficiently fast to offset other negative effects correlated with the surface characteristics of Cr-Cu/$SiCl_4$-Z catalyst. However, $SiCl_4$-Z showed improved hydrothermal and hydrogen chloride stabilities with a suppressed coking tendency. Cr-Cu/$SiCl_4$-Z catalyst also produced softer (less aromatic) coke in the combustion of ethyl acetate. This catalyst was less deactivated by chlorinated VOCs and, significantly more activity loss was experienced with TCE feed. In the combustion of chlorinated VOC, the deactivation was primarily attributed to the chlorination of active metal species rather than chemical changes on the surface of the catalyst support. The chlorination of metal species deactivated the catalyst by rendering lower redox ability. The result was in agreement with the Mars-van Krevelen model.

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